REMARKS

Entry of the foregoing, reexamination and reconsideration of the subject application, pursuant to and consistent with 37 C.F.R. § 1.111, are respectfully requested in light of the remarks which follow.

Applicants gratefully acknowledge the Examiner's determination that claims 6 and 7 contain allowable subject matter. *See* OFFICE ACTION at 2.

I. Amendments to the Claims

By the foregoing amendments to the claims, claim 3 is amended to correct a capitalization error in "HCl" and claim 6 has been amended to be in independent form. No new matter has been added.

II. Response to Objections to the Claims and Allowable Subject Matter

The Examiner has objected to claims 6 and 7 for being dependent upon a rejected base claim, but deemed them to be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. *See* OFFICE ACTION at 2.

Claim 6 is now in independent form. Claim 7 depends from claim 6. Accordingly, the objection to claims 6 and 7 is moot, and these claims are in condition for allowance for the reasons of record.

III. Response to Claim Rejection Under 35 U.S.C. § 103(a)

The Examiner has rejected claims 1-5 under 35 U.S.C. § 103(a) as purportedly being unpatentable over Reichmann et al ("Raman Study of the Preparation of SiO_2-supported TiO_2 from $TiCl_4$ and HCl," *Langmuir*, 1987, Vol. 3, pp. 111-116) (hereinafter, "Reichmann") with Jones et al. (U.S. Patent No. 5,024,827) (hereinafter, "Jones"), and optionally further in view of Jun-Jae Kim et al. ("Homogeneous Precipitation of TiO_2 Ultrafine Powders from Aqueous

TiOCL$_2$ Solution," *J. Am. Ceramic Society*, 1999, Vol. 82, No. 4, pp. 927-32) (hereinafter, "Kim"). *See* OFFICE ACTION at 3-5. The rejection is respectfully traversed.

It is elementary that to support an obviousness rejection, all of the claim limitations must be taught or suggested by the prior art as applied. *CFMT Inc. v. Yieldup International Corp.*, 68 USPQ2d 1940, 1947 (Fed. Cir. 2003).

Reichmann discloses a process for the preparation of titanium aquo-oxo chloride from a solution of 1.7 M TiCl$_4$ and 6.0 M HCl (p. 113, second column), or impregnation of silica with a 1.7M TiCl$_4$ and 6.0M HCl solution and subsequent evaporation of the solvent at 60°C (p. 114, first column).

Jones concerns a method for the preparation of titanium dioxide particles from a TiOCl$_2$ solution and discloses that a solution of TiOCl$_2$ can be obtained by hydrolyzing TiCl$_4$ in water acidified with hydrochloric acid (Example 1).

Kim describe a method for the preparation of TiO$_2$ from an aqueous solution of TiOCl$_2$. Kim teaches that, when a TiOCl$_2$ solution is used as starting material, TiO$_2$ is obtained at 100°C, whereas temperatures higher that 400°C are required when a TiCl$_4$ solution is used as starting material.

The claimed process differs from the one of Reichmann in that: (1) TiOCl$_2$ is hydrolysed, and not TiCl$_4$, and (2) the moisture content is specifically between 50 and 60%.

No TiOCl$_2$ Inherently Arises in Reichmann

The references as applied fail to disclose the claimed preparing titanium aquo-oxo chloride by hydrolyzing TiOCl$_2$ in an atmosphere with a moisture content is maintained between 50 and 60% or by an alkali metal carbonate A$_2$CO$_3$. The rejection relies on Jones (which discloses that a solution of TiOCl$_2$ can be obtained by hydrolyzing TiCl$_4$ in water

acidified with hydrochloric acid) for the contention that, under Reichmann's conditions, a $TiOCl_2$ solution is formed inherently.

Furthermore, while Jones discloses that a solution of $TiOCl_2$ can be obtained by hydrolyzing $TiCl_4$ in water acidified with hydrochloric acid, which is true, but only in very specific conditions, especially in presence of an inert gas (such as argon) and absolutely not when the $TiCl_4$ solution is in contact with air, i.e. in Reichmann's conditions. Thus, it is respectfully submitted that Jones is insufficient to establish that $TiOCl_2$ inherently occurs under the conditions of Reichmann, so that there is no teaching nor suggestion in Reichmann that conditions to form $TiOCl_2$ are carried out.

The References Fail to Disclose an Atmosphere with a Moisture Content Between 50 and 60%

Moreover, even if $TiOCl_2$ did arise in Reichmann (which has not been demonstrated), the references as applied fail to teach or suggest the claimed "atmosphere with a moisture content [that] is maintained between 50 and 60%." The rejection first contends that the water in Reichmann is "an atmosphere" and further contends that the moisture content would be easy to optimize for the skilled person.

In construing claims, "it would be unreasonable for the PTO to ignore any interpretive guidance afforded by the applicant's written description[.]" *In re Morris*, 127 F.3d 1048, 1054 (Fed. Cir. 1997). That is, the interpretation of the claim language must be "reasonable in light of the totality of the written description[.]" *In re Baker Hughes, Inc.*, 215 F.3d 1297, 1303 (Fed. Cir. 2000).

Here, the plain meaning of "atmosphere" notwithstanding, the specification clearly means for an atmosphere to refer to a gaseous atmosphere, not the solution of Reichmann. The specification, in referring to the claimed atmosphere with a moisture content of between

50 and 60% also uses the phrase "relative humidity." Specification, p. 4, lines 1-10. The rejection fails to explain how a solution might have a relative humidity, or how and why a person of ordinary skill in the art would replace a portion of Reichmann's solution to arrive at the claimed moisture content.

Furthermore, the rejection lacks a factual foundation for the contention that it would be obvious to optimize the moisture content. A particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation. *Ex Parte Whalen*, 89 USPQ2d 1078, 1084 (BPAI 2008) (citing *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977)); MPEP 2144.05.II.B. In this case, the record fails to indicate that one of ordinary skill in the art would recognize the claimed atmospheric moisture content as a variable to optimize. Instead, Reichmann varies the concentration of $TiCl_4$ (see Reichmann, p. 112, second column). None of the documents even suggest that the moisture content has an impact on the quality of the crystals (discussed below).

No Reason to Select $TiOCl_2$ instead of $TiCl_4$

The Examiner considers that, even is $TiOCl_2$ is not formed inherently, the claimed process is obvious in view of Reichmann and Jones over Kim, as the skilled person would use $TiOCl_2$ instead of $TiCl_4$ to save energy.

Applicants point out that it is well-known in the art that $TiCl_4$ hydrolyses into TiO_2 in a moist atmosphere, and not into $TiOCl_2$ (see the appended marked passages of the enclosed articles from Alyea, Zeatoun, and Wikipedia).

Regarding the argument concerning saving energy, please note that the temperatures carried out in Kim with $TiCl_4$ (400°C) are much higher than the one of Reichmann (60°C) and that a search for energy improvement is not particularly relevant for Reichmann's process.

Finally, Kim fails to cure the above-noted deficiencies of Reichmann and Jones with regard to the claimed atmospheric moisture content.

Superior and Unexpected Results

The claimed conditions lead to crystals of <u>improved quality</u> compared to those of Reichmann (*see* p. 3, lines 1-5 of the present application), said improved quality allowing an <u>improvement of efficacies in photocatalysis</u> when substrates are used, the surfaces of which are coated with the titanium aquo-oxo chloride according to the invention (*see* p. 3, lines 7-14 of the present application).

Evidence of unobvious or unexpected advantageous properties, such as superiority in a property the claimed compound shares with the prior art, can rebut *prima facie* obviousness. MPEP 716.02(a).II. The PTO must consider comparative data in the specification in determining whether the claimed invention is patentable. *In re Soni*, 34 USPQ2d 1684, 1687 (Fed. Cir. 1995).

The improvements arise from the two claimed features, namely:

(1) $TiOCl_2$ hydrolysis is slower than the one of $TiCl_4$, leading to crystals of <u>better quality,</u>

(2)   The specific moisture content is the one leading to <u>good quality</u> crystals obtainable in <u>reproducible</u> manner.

Such improvements are not suggested in the cited references.

First of all, the skilled person would have found no specific reason to make use of the method of Kim. Especially, there is no reason to select Kim to improve the quality of Reichmann's crystals, as Kim does not concern preparation of titanium aquo-oxo chloride. The skilled person would therefore not have used a $TiOCl_2$ solution as starting material.

For all of the above reasons, Applicants respectfully submit that the claims are nonobvious, and reconsideration and withdrawal of the rejection is requested.

CONCLUSION

In view of the foregoing, further and favorable action in the form of a Notice of Allowance is believed to be next in order. Such action is earnestly solicited.
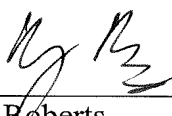
In the event that there are any questions relating to this Amendment and Reply, or the application in general, it would be appreciated if the Examiner would telephone the undersigned attorney concerning such questions so that prosecution of this application may be expedited.

Respectfully submitted,

BUCHANAN INGERSOLL & ROONEY PC

Date: May 27, 2010   By: _____
                                  Roy Roberts
                                  Registration No. 54402

Customer No. 21839
703 836 6620

20. GROUP VII. THE HALOGENS

E. Iodine

Dem. 625—Iodide in Iodized Salt

Experiment developed by Raymond P. Garman.

To show: The presence of iodine ion in iodized salt.

Materials: Morton's iodized salt, Cl_2-aq, starch-aq, CS_2, H-3.

Procedure: (a) Dissolve 3 g iodized salt in 10 ml water; project in culture tube in H-3. Add 1 drop Cl_2-aq, shake vigorously (if the solution is not slightly brown now, add a second drop of Cl_2 and shake; however do not add too much Cl_2). Pour half of the solution into a second culture tube. Project both tubes in H-3. (b) To one add 5 ml CS_2 (CARE: fire hazard) and shake. (c) To the other add 5 ml starch-aq and shake.

Observations: (a) The small amount of I^- in the salt is liberated as I_2 by the Cl_2-aq; this colors the solution faintly brown. (b) The CS_2 concentrates the I_2 to form a pink (dilute) to purple (conc.) solution. (c) The starch-aq forms blue starch-iodine.

Dem. 626—Starch in Potatoes

Experiment developed by Raymond P. Garvin.

To show: That potatoes contain starch.

Materials: Potato, knife, mortar and pestle, tincture of iodine, C-2 filter paper, funnel.

Procedure: Grind a slice of potato with 20 ml of water, and filter to give a clear extract. Project C-2 with one cell three-quarters full of water and cell *2* ³/₄ full of the potato extract. Add one drop (only) of tincture of iodine to each.

Observations: The solution in cell *1* is slightly yellow; in cell *2* the iodine forms a blue compound with the potato starch.

Dem. 627—Secret Writing (KI + Cl₂-gas)

Experiment developed by Raymond P. Garman.

To show: KI-ink writing developed by Cl_2-gas.

Materials: A 5 × 4-in. sheet of cellophane; KI-aq, cotton-tipped swab, Cl_2-gas, C-1, detergent.

Procedure: Using the swab as a pen and KI-aq as ink, write a "secret message" on the cellophane sheet. Drop it into C-1 and project. Dry thoroughly until it is invisible. Drop it into C-1 and project. Now blow Cl_2 gas into the cell.

Observations: The chlorine brings out the invisible writing as brown I_2. Reaction $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$ (brown).

Note: Glass plate may be used in place of cellophane. Add soap or other wetting agent to KI solution to aid in writing on glass or cellophane.

Dem. 628—Secret Writing (KI + Starch-aq + Cl₂-aq)

To show: Secret writing with KI-aq developed by Cl_2-aq + starch-aq.

Materials: A 4 × 4-in. sheet of cellophane cotton-tipped swab, 5 ml KI-aq + 2 g starch, C-1, Cl_2-aq.

Procedure: Using the swab as a pen and KI + starch as ink, write a "secret message" on the cellophane. Dry slightly. Project C-1 ²/₃ full of water to which dropperfuls of Cl_2-aq have been added. Dip the sheet into the solution.

Observations: The chlorine liberates iodine, which colors the starch blue: the writing appears darkly on the screen.

Dem. 629—Secret Writing (Starch + Iodine)

To show: Secret writing with starch developed by iodine.

Materials: A 4 × 4-in. cellophane sheet; starch-aq, tincture of iodine, cotton-tipped swab.

Procedure: Using the swab as a pen, and the starch-aq as ink, write a "secret message" on the cellophane. Let dry somewhat. Project C-1 ²/₃ full of water. Put the cellophane in C-1, then add two drops of tincture of iodine.

Observations: The "secret writing" appears blue as the iodide-starch complex is formed.

Note: Glass plate may be used in place of cellophane.

21. METALS OF GROUPS IV-VIII.

A. Group IV. (Ti, Sn, Pb)

Dem. 630—TiCl₄ Hydrolysis

To show: The hydrolysis of titanium tetrachloride.

Materials: Wide-mouth 2-oz. square bottle with 2-hole stopper, inlet and outlet tubes 2 in. long with 1-ft. rubber tubing each; $TiCl_4$.

Procedure: Project; blow gently into rubber tubing leading into bottle containing 2 ml $TiCl_4$.

Observations: Smoke clouds of TiO_2 from hydrolysis of $TiCl_4$ with moisture in the air.

Dem. 631—Spongy Tin

Experiment developed by Kenneth V. Jackman.

To show: The formation of spongy tin.

Materials: $SnCl_2 \cdot 2H_2O$, 6 M HCl, 20-mesh Zn, C-2.

Procedure: Project 1 g $SnCl_2 \cdot 2H_2O$ + 20 ml H_2O +

Characterization of TiO₂ Smoke Prepared Using Gas-Phase Hydrolysis of TiCl₄

Lua'y Zeatoun*, Donald Feke**

Abstract

The formation of submicron TiO₂ smoke (a gas-phase suspension) from titanium tetrachloride in a low-pressure hydrolysis reaction in a simple reactor configuration has been studied. Particle size distribution, particle morphology and degree of crystallinity have been characterized as a function of reaction conditions. Highly crystalline anatase TiO₂ particles with narrow size distribution and smaller particle size were formed at high reactor temperature, while larger, amorphous particles were found at lower reactor temperatures. These results are consistent with literature studies. At 817 °C, small (450 nm), spherical, unagglomerated particles could be produced. A gas-phase dispersion of these particles is intended for use as seeds in subsequent kinetic studies of titanium dioxide formation reactions involving a rapid compression methodology.

Keywords: aerosol, hydrolysis, titanium dioxide

1 Introduction

Titanium dioxide (titania, TiO₂) can be found in nature in a pure enough crystalline state to be used as gemstones. However, micron and submicron particulate titania is the form most commonly used in commercial practice. Titania powders are widely used as pigments because of their high light scattering ability with almost no absorbance in the visible range. Titania is also used to a large extent in plastics, cosmetics, catalysts, ceramic membranes, and many other applications [1]. This widespread use of titania is attributed to the favorable properties it imparts, such as strength, durability, chemical inertness, UV absorption and high dielectric constant. Titania has three crystallographic forms; anatase, rutile, and brookite [2]. Rutile TiO₂ has higher refractive index, UV absorption and stronger mechanical durability resistance than other forms of titania. Rutile is the most thermo-chemically stable phase and is the crystal structure preferred for high UV absorptivity. Depending on the particular application, the particle size of TiO₂ may need to be controlled within very narrow limits, so researchers have studied the relationship between synthesis conditions, particle size and the relative selectivity of anatase versus rutile TiO₂ [3–5]. The rutile phase is typically formed at higher reaction temperatures than the anatase phase.

Titania powders can be produced by oxidizing volatile metal chlorides (e.g., TiCl₄) at high temperature using industrial flame-aerosol reactors and near atmospheric pressure [6–8]. In flame synthesis, the formation of titania particles starts from the homogeneous nucleation of a stable cluster of gaseous molecules of TiO₂. Subsequently, repeated condensation of additional molecules onto the surface of the growing cluster occurs until the final size is reached. These steps may be represented by the reactions [5]:

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(g) + 2Cl_2 \qquad (1)$$

$$nTiO_2(g) \rightarrow (TiO_2)_n(s). \qquad (2)$$
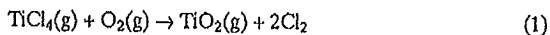
The oxidation rate of TiCl₄ vapor has been found to be first order with respect to TiCl₄ and to follow the Arrhe-
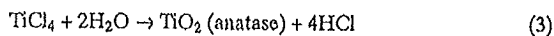
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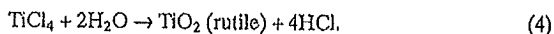   E-mail: donald.feke@case.edu

nius equation [9]. Since the titania powders are formed in the vapor phase, many interconnected phenomena affect the particle morphology. These include the chemical reaction pathways (gas phase and/or surface), nucleation type (homogeneous and heterogeneous), transport effects (which can lead to particle agglomeration or deposition onto surfaces), and sintering. The ultimate particle size depends on these factors as well [10]. In addition, hydrolysis and oxidation of $TiCl_4$ are competing effects that might also occur at lower reaction temperatures and may affect the particle shape and crystalline phase of the titania powder [11]. Also, particle growth can be influenced by a surface reaction that gives a size distribution narrower than the typical self-preserving one observed when the conversion is below 99 % [12].

Although some studies have been reported in the literature, e.g. [13], the effects of reaction temperature and gas composition on the particle size are not yet fully understood. Despite these uncertainties, flame synthesis of titania is performed at a rate of about 100 ton/day [14–16].

Titania can also be formed from a liquid-phase hydrolysis reaction, and this route has also been used commercially to manufacture TiO_2 in fine particulate form. $TiCl_4$ is soluble in cold water, and the hydrolysis reaction proceeds rapidly at mild temperatures. The overall reaction chemistry is:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 \text{ (anatase)} + 4HCl \qquad (3)$$

or

$$TiCl_4 + 2H_2O \rightarrow TiO_2 \text{ (rutile)} + 4HCl. \qquad (4)$$

The two reactions can occur in parallel, but reaction (4) is more thermodynamically favorable [17].

Raghavan [18] has measured the kinetics of $TiCl_4$ oxidation at high temperatures using a rapid compression machine (RCM). The heart of this reactor is a cylinder containing a gas mixture (typically 1 % O_2 + 0.3 % $TiCl_4$ in Ar). Using a quickly moving piston, this mixture is rapidly compressed causing the gas temperature to rise,

which triggers the reactions. Particulate TiO_2 was formed according to the homogenous kinetics given by reactions (1) and (2). Ultimately, we plan to extend this work to study the case of heterogeneous nucleation in RCM processing. For this purpose, submicron-sized TiO_2 particles in a gas-phase dispersion will be seeded into the reactor before compression is applied. The resulting reaction kinetics for the formation of the titania particles should depend on the characteristics and quantity of seed material used in the RCM experiments. Thus, controlling the composition and morphology of the seed particles will be fundamental to the success of this envisioned synthesis pathway.

For the purpose of synthesizing aerosol dispersions of the seed particles, we constructed a small reaction chamber for the production of TiO_2 smokes through the gas-phase hydrolysis of $TiCl_4$. The goal of the present study is to determine the effect of reaction temperature on the particle size, morphology and state of crystallinity of the TiO_2 particles produced in this simple smoke chamber. A secondary goal is to demonstrate that submicron sized solids in an aerosol suspension could be produced consistently in a relatively simple experimental procedure.

2 Experimental

2.1 Apparatus

Figure 1 shows a schematic of the experimental apparatus. This consists of a reservoir for the liquid $TiCl_4$ (a glass tube, MDC, SEG-075, ID 14.3 mm, and length 111 mm) with a flange of 33.8 mm connected to 6.2 mm stainless-steel line, pressure transducer, vacuum pump, and reactor vessel (a 250 ml three-neck round-bottom glass flask). The reservoir for liquid $TiCl_4$ (99.9 % purity Aldrich) was filled within a glove box (pure Ar environment) to prevent any moisture contacting the $TiCl_4$. Heating tape wrapped around the reservoir maintained the liquid $TiCl_4$ at 120 °C. All transfer lines were similarly heated to prevent any $TiCl_4$ condensation. The pro-
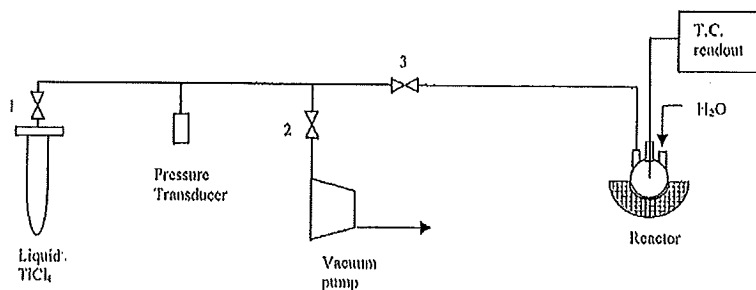

Fig. 1: Schematic of the experimental set-up for the preparation of TiO_2 smoke.

http://www.ppsc.com

duct gases were collected into a vent duct through a hose connected to the exhaust of the vacuum pump.

The reactor was warmed using a heating mantle, and the temperature was monitored using a thermocouple that sensed the external surface temperature of the vessel. For convenience, we refer to this temperature as the reactor temperature. Measurements showed that the internal contents of the reactor vessel could be maintained within 10 °C of the external surface temperature of the reactor.

2.2 Experimental Procedure

Prior to a synthesis experiment, a TEM grid was inserted inside the reaction vessel. By closing valve 1 and opening valves 2 and 3, the reactor and all lines could be evacuated using the 0.1 Torr vacuum pump. After closing valve 2 and opening valve 1, the reactor was filled with TiCl$_4$ vapor to a pressure of 60 Torr with the heater set point at 120 °C (internal reactor temperature of 110 °C). Excess TiCl$_4$ vapor was then purged from the lines by closing valves 1 and 3 and reopening valve 2 to the vacuum pump. Based on the known reactor volume, pressure, and temperature, the amount of TiCl$_4$ contained within the reactor could be calculated.

For the synthesis experiments, the reactor temperature was adjusted between 210 and 817 °C. However, to ensure that all of the water was consumed in the reaction, only 85 % of the stoichiometric amount of water (about 19.2 µl) was used. With the aid of a 100-µl syringe, this amount of saturated liquid water at 100 °C was injected gradually (over a span of 20 s) to the reactor in order to control the pressure rise as the reaction proceeds. The formation of a turbid aerosol occurred immediately as the water was being injected. Due to the reaction exotherm, the reactor contents increase in temperature, but measurement showed this increase to be relatively small (typically 2–3 °C) and negligible relative to the span of temperatures studied.

Although some TiO$_2$ particles adhered to the inner surfaces of the reactor, a substantial amount remained suspended in the gas phase. Immediately after the total amount of water was injected, one port on the reactor vessel was opened to the atmosphere. A second TEM grid held by tweezers was quickly placed in the path of the exiting smoke. The location of the second TEM grid was next to the tip of the flask neck and this distance was held fixed for all the experimental runs. Both this grid and the one recovered from the inside of the reactor

were taken for imaging. Typically, smoke continued to stream from the reactor vessel for several minutes after it was opened to the atmosphere.

2.3 Characterization

Reaction products were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), and light scattering. XRD measurements were carried out on SCINTAG-XGEN 4000 X-ray diffractometer using CuKα radiation. TEM images were taken using a Philips-CM20 electron microscope.

The titania powder remaining in the reaction vessel after the smoke cleared was suspended in deionized water through the use of a high-power ultrasonic probe (Misonix-XL2020). Particle size analysis was measured using a Malvern ZetaMaster instrument. The Zetamaster combines the advantages of a heterodyne laser Doppler electrophoresis system and a separate fixed 90° optical scattering system for size measurements.

3 Results and Discussion

Figures 2–5 show TEM images of the TiO$_2$ particles formed at four different reactor temperatures. In each figure appear one image of the particles captured from the titania smoke stream released from the reactor and a second image of those particles that settled within the reaction vessel. In all cases, the primary particles are seen to be quite small (typically below 100 nm). However, in most cases the particles are observed to have formed extended, open-structured clusters. This morphology is characteristic of a fast agglomeration process. The two sets of images within Figures 2–4 show very
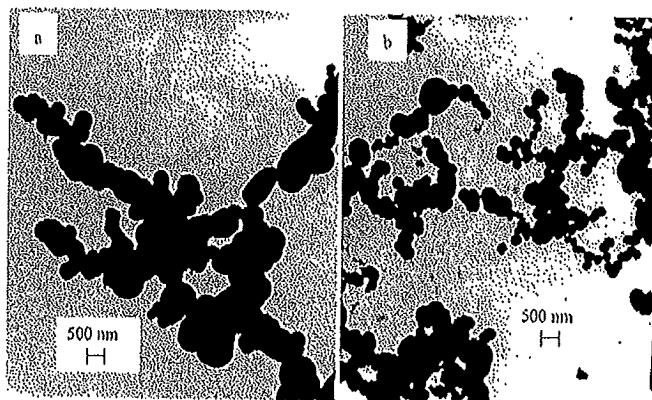

Fig. 2: Transmission electron micrographs of titania formed at a reactor temperature of 210 °C; (a) smoke stream and (b) powder settled after reaction.
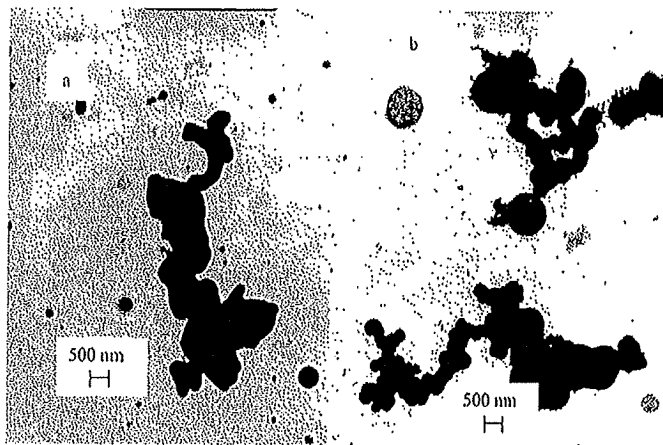
Fig. 3: Transmission electron micrographs of titania formed at a reactor temperature of 322 °C; (a) smoke stream and (b) powder settled after reaction.
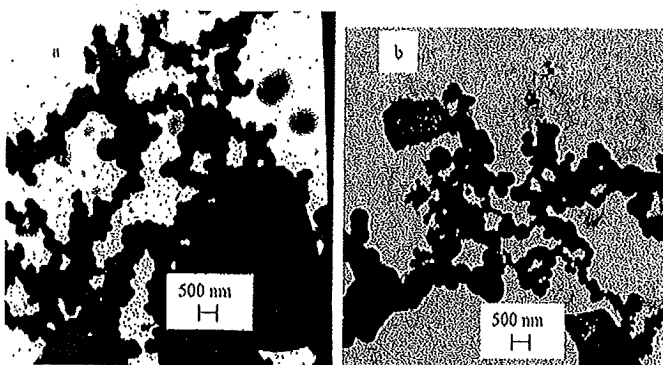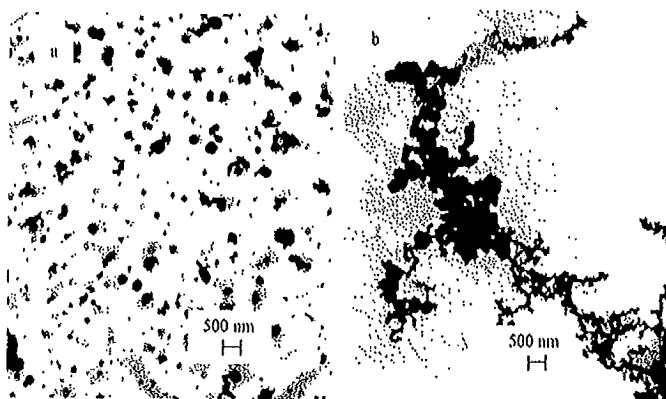

Fig. 4: Transmission electron micrographs of titania formed at a reactor temperature of 405 °C; (a) smoke stream and (b) powder settled after reaction.

Fig. 5: Transmission electron micrographs of titania formed at a reactor temperature of 817 °C; (a) smoke stream and (b) powder settled after reaction.

similar trends with reactor temperature, both in terms of cluster morphology and size. Thus, samples taken from the reactor vessel for particle-size analysis are believed to give results that would be representative of the actual particle-size within the smoke stream.

The results obtained at 817 °C show a different trend. Spherical, unagglomerated particles were observed in the gas-phase sample. In this case, the particles appear to be smaller than those produced at the lower temperatures, but the primary particles have a rather wide variation in size (25–250 nm). The fine-structure of the clusters observed in the samples recovered from inside the reactor also reflects this small primary-particle size.

Figure 6 summarizes the measurements of the size of particles recovered from the reactor vessel. It is found that the mean of the particle size either by intensity, volume, or number is almost the same indicating a narrow size distribution. There is a clear trend that increasing the reactor temperature results in a decrease in the average cluster size of the titania powder. Figure 6 represents the results of ten measurements, and the deviation for these runs was found to be varying between 20–55 nm.

We note that the clusters depicted in the TEM images are typically larger than the results indicated in Figure 6. This difference can be attributed to the sample preparation process for the particle size analysis, in which intense sonication is used to disperse the titania clusters into water. Clearly, the sonication is capable of breaking down the clusters shown in the TEM images. Figure 7 shows the particle size distribution for the particles prepared using different reactor temperatures, it indicates that the average particle size increases with decreasing the reactor temperature. The size distribution is quite narrow, and this was typical of the powders produced at the other temperatures as well.

The results from the XRD studies are summarized in Figure 8. For the low range of reactor temperatures studied (182–322 °C), the powder samples exhibited an amorphous structure. For the higher temperature range (405–817 °C), six intense diffraction peaks appeared ($2\theta = 25.9°$, $38.6°$,
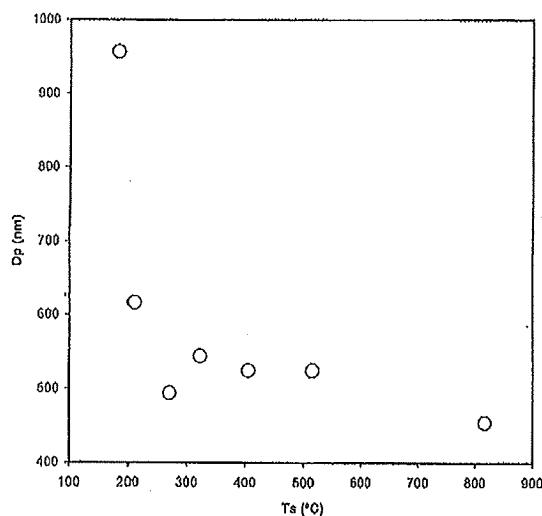
Fig. 6: Effect of reactor temperature on the average particle diameter of titania powder settled at the bottom of the reactor measured using the particle-size analyzer.
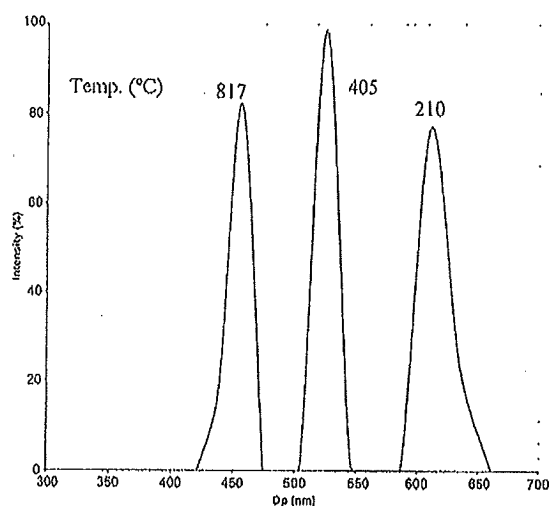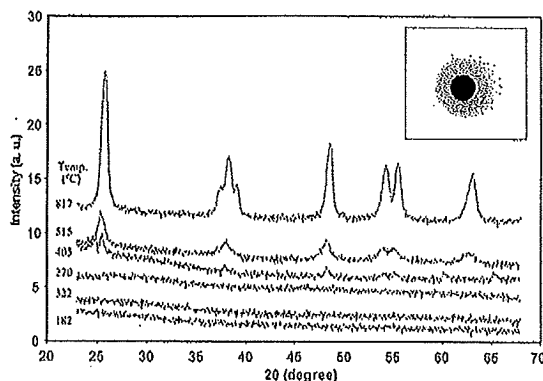

Fig. 8: X-ray diffraction patterns of the titania powder formed at different temperatures which settled within the reactor. The inset shows the diffraction image obtained at 817 °C.

enhanced kinetics of anatase nucleation relative to the growth step at the higher temperatures. With a greater number of nuclei present and a fixed amount of TiO_2 present the reactor, the growth of individual particles is limited. On the other hand, in some cases the opposite trend of particle size increasing with reaction temperature can be encountered when coalescence and/or sintering is the controlling step [19–21]. Higher temperatures result in higher rates of particle sintering, and consequently larger clusters are produced. Akhtar et al. [11] showed that rate of oxidation of $TiCl_4$ is higher than the rate of hydrolysis at higher reactor temperature resulting in a decrease of the average particle size. This also might explain the resulting smaller particle size where oxidation mechanism is more favorable at higher temperatures. One challenge is to strike a balance between these effects in order to gain control over the particle size distribution.

Fig. 7: Particle size distribution of titania powder settled at different surface temperatures using the particle-size analyzer.

48.6°, 54.4°, 55.6°, and 63.1°) which correspond to the diffraction peaks of anatase TiO_2. The XRD spectra show no evidence of the formation of rutile titania. The inset within Figure 8 shows the diffraction patterns of titania powder formed at a reactor temperature of 817 °C confirming the crystalline structure of this sample.

Our results are largely consistent with that of other researchers [5,11,13]. The trend of decreased particle size with reactor temperature and can be attributed to the

4 Conclusions

In summary, the preparation of titania smoke by the gas-phase hydrolysis of $TiCl_4$ in a relatively simple experimental approach has been investigated as a function of reaction temperature. Substantial amounts of small, submicron particles that remain dispersed in the gas-phase have been observed. Powder that settles within the reaction vessel typically exhibits open-structured agglomerates that, upon sonication and dispersion into water, have narrow size distribution. The anatase form of titania was observed for the powders prepared at the higher temperatures studies, while amorphous powders resulted when lower reactor temperatures were used. At 817 °C, the gas-phase aerosol was seen to consist of un-

agglomerated, spherical particles having a relatively wide size distribution.

Although this experimental approach for producing seed particles was performed under non-ideal conditions in a fairly simple apparatus, we are encouraged that this method produces results that are reproducible and interpretable relative to existing literature.

5 Acknowledgements

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Titanium tetrachloride

From Wikipedia, the free encyclopedia

Titanium tetrachloride is the inorganic compound with the formula $TiCl_4$. It is an important intermediate in the production of titanium metal and the pigment titanium dioxide. $TiCl_4$ is an unusual example of a metal halide that is highly volatile. Upon contact with humid air, it forms spectacular opaque clouds of titanium dioxide (TiO_2) and hydrogen chloride (HCl). An alterntive IUPAC name is *tetrachlorotitanium*.
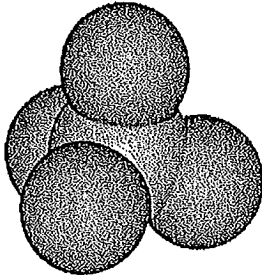
Contents

Properties and structure

$TiCl_4$ is a dense, colourless distillable liquid, although crude samples may be yellow or even red-brown. It is one of the rare transition metal halides that is a liquid at room temperature, VCl_4 being another example. This property reflects the fact that $TiCl_4$ is molecular; that is, each $TiCl_4$ molecule is relatively weakly associated with its neighbours. Most metal chlorides are polymers, wherein the chloride atoms bridge between the metals. The attraction between the individual $TiCl_4$ molecules is weak, primarily van der Waals forces, and these weak interactions result in low melting and boiling points, similar to those of CCl_4.

Ti^{4+} has a "closed" electronic shell, with the same number of electrons as the inert gas argon. The tetrahedral structure for $TiCl_4$ is consistent with its description as a d^0 metal center (Ti^{4+}) surrounded by four identical ligands. This configuration leads to highly symmetrical structures, hence the tetrahedral shape of the molecule. $TiCl_4$ adopts similar structures to $TiBr_4$ and TiI_4; the three compounds share many similarities. $TiCl_4$ and $TiBr_4$ react to give mixed halides $TiCl_{4-x}Br_x$, where x = 0, 1, 2, 3, 4. Magnetic resonance measurements also indicate that halide exchange is also rapid between $TiCl_4$ and VCl_4.[1]

$TiCl_4$ is soluble in toluene and chlorocarbons, as are other non-

Titanium tetrachloride

IUPAC name	
Titanium tetrachloride	
Titanium(IV) chloride	
Identifiers	
CAS number	7550-45-0
PubChem	24193
EC number	231-441-9
UN number	1838
RTECS number	XR1925000
Properties	
Molecular formula	$TiCl_4$
Molar mass	189.71 g/mol
Appearance	colourless fuming liquid
Density	1.726 g/cm³
Melting point	-24.8 °C
Boiling point	136.4 °C
Solubility in water	reacts to form TiO_2 and HCl
Solubility	soluble in ethanol
Viscosity	8.27×10^{-4} Pa·s
Structure	
Molecular shape	Tetrahedral
Dipole moment	zero
Thermochemistry	
Std enthalpy of formation $\Delta_f H^\circ_{298}$	-804.16 kJ/mol
Standard molar entropy S°_{298}	221.93 $JK^{-1}mol^{-1}$
Hazards	
MSDS	MSDS
EU Index	022-001-00-5
EU classification	Corrosive (C)
R-phrases	R14, R34
S-phrases	(S1/2), S7/8, S26, S36/37/39, S45
NFPA 704	
Flash point	Non-flammable
Related compounds	
Other anions	Titanium(IV) fluoride

polar species. Evidence exists that certain arenes form complexes of the type $[(C_6R_6)TiCl_3]^+$. $TiCl_4$ reacts exothermically with donor solvents such as THF to give hexacoordinated adducts.[2] Bulkier ligands (L) give pentacoordinated adducts $TiCl_4L$.

Other cations	Titanium(IV) bromide
	Titanium(IV) iodide
	Zirconium(IV) chloride
	Hafnium(IV) chloride
Related compounds	Titanium(II) chloride
	Titanium(III) chloride

✓ (what is this?) (verify)

Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)

Infobox references

Production

$TiCl_4$ is produced by the chloride process, which involves the reduction of titanium oxide ores, typically ilmenite ($FeTiO_3$) with carbon under flowing chlorine at 900 °C. Impurities are removed by distillation.

$$2 FeTiO_3 + 7 Cl_2 + 6 C \rightarrow 2 TiCl_4 + 2 FeCl_3 + 6 CO$$
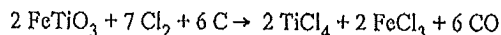
The coproduction of $FeCl_3$ is undesirable, which has motivated the development of alternative technologies. Instead of directly using ilmenite, "rutile slag" is used. This material, an impure form of TiO_2, is derived from ilmenite by removal of iron, either using carbon reduction or extraction with sulfuric acid. Crude $TiCl_4$ contains a variety of other volatile halides, including vanadyl chloride ($VOCl_3$), silicon tetrachloride ($SiCl_4$), and tin tetrachloride ($SnCl_4$), which must be separated.

# Applications

Production of titanium metal

The world's supply of titanium metal, about 4M tons per year, is made from $TiCl_4$. The conversion takes place by the reduction of the chloride with magnesium metal give titanium metal and magnesium chloride. This procedure is the final step of the Kroll process:

$$2 Mg + TiCl_4 \rightarrow 2 MgCl_2 + Ti$$
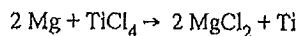
Liquid sodium has also been used instead of magnesium as the reducing agent.

Production of titanium dioxide

Around 90% of the $TiCl_4$ production is used to make the pigment titanium dioxide (TiO_2). The conversion involves hydrolysis of $TiCl_4$, a process that forms hydrogen chloride:[3]
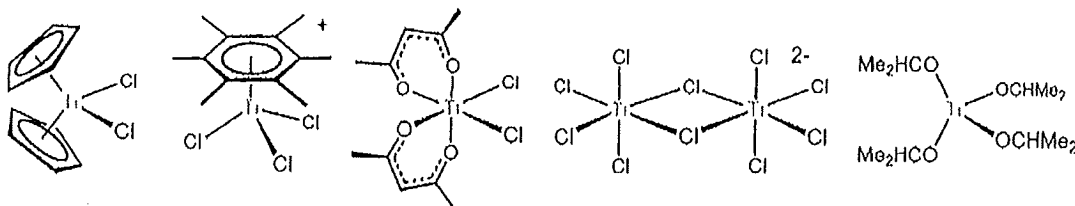
$$TiCl_4 + 2 H_2O \rightarrow TiO_2 + 4 HCl$$
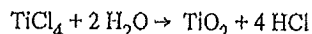
In some cases, $TiCl_4$ is oxidised directly with oxygen:

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2 Cl_2$$
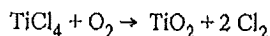
Chemical reactions

Titanium tetrachloride is a versatile reagent that forms diverse derivatives including those illustrated below.

### Hydrolysis and related reactions

The most noteworthy reaction of $TiCl_4$ is its easy hydrolysis, signaled by the release of corrosive hydrogen chloride and the formation of titanium oxides and oxychlorides, as described above for the production of TiO_2. In the past titanium tetrachloride has also been used to create naval smokescreens. The hydrogen chloride immediately absorbs more water to form tiny droplets of hydrochloric acid, which (depending on humidity) may absorb still more water, to produce large droplets that efficiently scatter light. In addition, the highly refractive titanium dioxide is also an efficient light scatterer. Because of the corrosiveness of its smoke, however, $TiCl_4$ is no longer used.

Alcohols react with $TiCl_4$ to give the corresponding alkoxides with the formula $[Ti(OR)_4]_n$ (R = alkyl, n = 1, 2, 4). As indicated by their formula, these alkoxides can adopt complex structures ranging from monomers to tetramers. Such compounds are useful in materials science as well as organic synthesis. A well known derivative is titanium isopropoxide, which is a monomer.

Organic amines react with $TiCl_4$ to give complexes containing amido (R_2N^--containing) and imido (RN^{2-}-containing) complexes. With ammonia, titanium nitride is formed. An illustrative reaction is the synthesis $Ti(NMe_2)_4$, a yellow, benzene-soluble liquid:[4] This molecule is tetrahedral, with planar nitrogen centers.[5]

$$4\ LiNMe_2 + TiCl_4 \rightarrow 4\ LiCl + Ti(NMe_2)_4$$
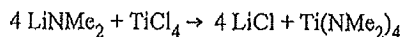
Complexes with simple ligands

$TiCl_4$ is a Lewis acid as implicated by its tendency to hydrolyze. With the ether THF, $TiCl_4$ reacts to give yellow crystals of $TiCl_4(THF)_2$. With chloride salts, $TiCl_4$ reacts to form sequentially $[Ti_2Cl_9]^-$, $[Ti_2Cl_{10}]^{2-}$ (see figure above), and $[TiCl_6]^{2-}$.[6] Interestingly, the reaction of chloride ions with $TiCl_4$ depends on the counterion. NBu_4Cl and $TiCl_4$ gives the pentacoordinate complex NBu_4TiCl_5, whereas smaller NEt_4^+ gives $(NEt_4)_2Ti_2Cl_{10}$. These reactions highlight the influence of electrostatic forces on the structures of compounds with highly ionic bonding.

Redox

Reduction of $TiCl_4$ with aluminium results in one-electron reduction. The *trichloride* ($TiCl_3$) and tetrachloride have contrasting properties: the trichloride is a solid, being a coordination polymer, and is paramagnetic. When the reduction is conducted in THF solution, the Ti(III) product converts to the light-blue adduct $TiCl_3(thf)_3$.

Organometallic chemistry

Main article: Organotitanium compound

The organometallic chemistry of titanium typically starts from $TiCl_4$. An important reaction involves sodium cyclopentadienyl to give titanocene dichloride, $TiCl_2(C_5H_5)_2$. This compound and many of its derivatives are precursors to Ziegler-Natta catalysts. Tebbe's reagent, useful in organic chemistry, is an aluminium-containing derivative of titanocene that arises from the reaction of titanocene dichloride with trimethylaluminium. It is used for the "olefination" reactions.

Arenes, such as $C_6(CH_3)_6$ react to give the piano-stool complexes $[Ti(C_6R_6)Cl_3]^+$ (R = H, CH_3; see figure above).[7] This reaction illustrates the high Lewis acidity of the $TiCl_3^+$ entity, which is generated by abstraction of chloride from $TiCl_4$ by $AlCl_3$.

Reagent in organic synthesis

$TiCl_4$ finds limited but diverse use in organic synthesis, capitalizing on its Lewis acidity and its oxophilicity.[8] Illustrative is the Mukaiyama aldol reaction. Key to this application is the tendency of $TiCl_4$ to activate aldehydes (RCHO) by formation of adducts such $(RCHO)TiCl_4OC(H)R$. It is also used in the McMurry reaction in conjunction with zinc, $LiAlH_4$. These reducing agents generate Ti(III) derivatives that couple ketones, leading to alkenes.

Toxicity and safety considerations

Hazards posed by titanium tetrachloride generally arise from the release of hydrogen chloride (HCl). $TiCl_4$ is a strong Lewis acid, exothermically forming adducts with even weak bases such as THF and explosively with water, releasing HCl.

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